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Spectrophotometric Determination of Formation Constants of Molecular Complexes

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A new model has been suggested for the determination of equilibrium constants, K_1, and extinction coefficient, ε, of fairly strong 1:1 molecular complexes. The model involves the assumption: $A/C_D^0 = K_1C_A^0\varepsilon/(1+K_1C_A^0)-K_1A/(1+K_1C_A^0)^2$, where A is the absorbance of the complex, and C_A^0 and C_D^0 are the initial concentration of the acceptor and donor respectively.

SEVERAL graphical approaches exist for evaluating the equilibrium constant (K_1) and extinction coefficient (ϵ) of 1:1 molecular complexes from spectrophotometric data in inert solvents[1-3]. Inherent, in all the derivations, is the assumption that if $C_D^0 \gg C_A^0 > C_{AD}$ (where C_A^0 and C_D^0 represent the initial concentrations of acceptor, A, and donor, D, respectively, and C_{AD} is the equilibrium concentration of the complex) then C_{AD} can be neglected in the term $(C_D^0 - C_{AD})$, in the expression for equilibrium constant (Eq. 2). However, this is not always a valid assumption. It has been noticed that this approximation fails in the case of strong molecular complexes, when $C_A^0 \approx C_{AD}$[4]. In such cases, neglecting the term C_{AD} will lead to erroneous equilibrium constants and other related thermodynamic data. We suggest a more adequate model than the ones presently used for the determination of K_1 and ϵ of fairly strong molecular complexes.

Theoretical

Under the conditions of equilibrium for 1:1 complex, AD, we have

$$A + D \rightleftharpoons AD;\ K = K_1K_\gamma;\ K_\gamma = \gamma_{AD}/\gamma_A\gamma_D \qquad ...(1)$$

and

$$K_1 = \frac{C_{AD}}{(C_A^0 - C_{AD})(C_D^0 - C_{AD})} \qquad ...(2)$$

where γ_i is the Raoult activity coefficient of species i. In general, K_1 and K_γ are not constants but are functions of concentrations of the reactants and products. Since in most spectrophotometric measurements, we keep C_A^0 constant and vary C_D^0, it is convenient to define a set of dimensionless quantities as follows:

$$K_1^* = K_1C_A^0;\ C_D^{0*} = C_D^0/C_A^0;\ C_{AD}^* = C_{AD}/C_A^0$$

In terms of these dimensionless quantities, Eq. (2) becomes

$$K_1^* = \frac{C_{AD}^*}{(1 - C_{AD}^*)(C_D^{0*} - C_{AD}^*)} \qquad ...(3)$$

Solving for C_{AD}^* from Eq. 3 yields

$$C_{AD}^* = 1/2(1 + C_D^{0*} + 1/K_1^*) - 1/2[(1 + C_D^{0*} + 1/K_1^*)^2 - 4C_D^{0*}]^{\frac{1}{2}}$$

$$= \sum_{k=1}^{\infty} \frac{(2k-2)}{k!.(k-1)!} \frac{C_D^{0*k}}{(1 + C_D^{0*} + 1/K_1^*)^{2k-1}}$$

$$= \frac{C_D^{0*}}{(1 + C_D^{0*} + 1/K_1^*)}\left[1 + \frac{C_D^{0*}}{(1 + C_D^{0*} + 1/K_1^*)^2}\right] + \ldots\ldots \qquad ...(4)$$

Eq. (4) indicates that when $C_D^{0*} \ll 1/K_1^*$ C_{AD}^* varies linearly with C_D^{0*}. Fig. 1 shows the theoretical plots between C_{AD}^* and C_D^{0*} for different K_1^* values. These plots indicate that the linear relation between C_{AD}^* and C_D^{0*} holds only up to $K_1^* = 10^{-3}$.

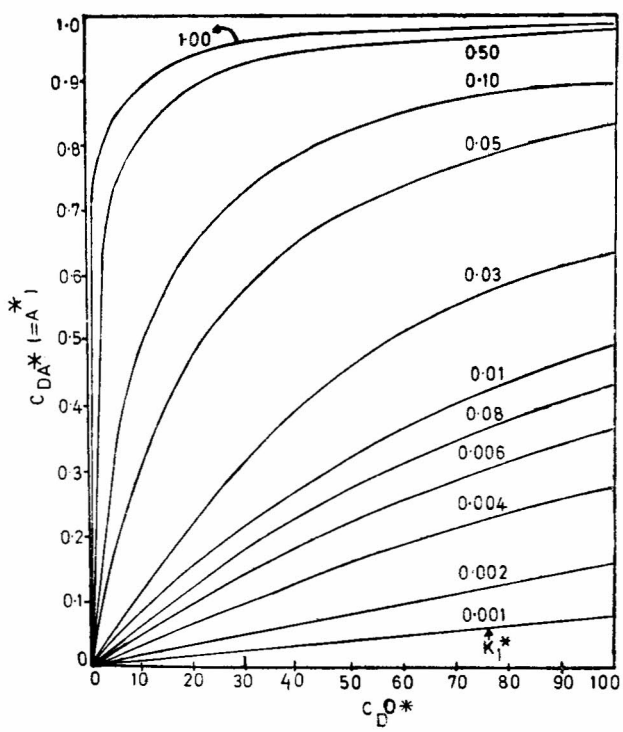

Fig. 1 — Theoretical plot of C_{DA}^* (= A^*) versus C_D^{*0} for different values of K_1^*

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The Beer-Lambert law can be stated as $A = \epsilon l C_{AD}$ (where A is the absorbance, ϵ is the molar extinction coeffiient and l is the path length). Assuming that $l = 1$ cm, we have

$$C^*_{AD} = \frac{A}{\epsilon C^0_A} = A^* \qquad ...(5)$$

Eq. 5 indicates that C^*_{AD} is proportional to A^*. Thus, if we draw a theroetical plot of log A^* (or log C^*_{AD}) versus log C^{0*}_D for various values of K^*_1, then by superimposing on it an experimental plot of log A versus log C^0_D we can determine K^*_1 and hence K_1. Eq. 5 shows that A is always smaller than ϵC^0_A. Substitution of Eq. (5) into Eq. (3) gives Eq. (6).

$$K^*_1 = \frac{A^*}{(1-A^*)(C^{0*}_D - A^*)} = \frac{A^*/C^{0*}_D}{(1-A^*)(1-A^*/C^{0*}_D)} \qquad ...(6)$$

If we choose $C^{0*}_D \gg 1$ (i.e. $C^{0*}_D \gg C^0_A$), then $A^*/C^{0*}_D \ll 1$, and Eq. 6, after neglecting A^*/C^{0*}_D, reduces to Eq. 7,

$$A^*/C^{0*}_D = K^*_1(1-A^*) \qquad ...(7)$$

which is of the same form as Benesi-Hildebrand (BH)[1], Scott[2] or Foster-Hammick-Wardley (FHW)[3] equations.

To find out the exact linear relation between A^*/C^{0*}_D and A^*, we rewrite Eq. (6) as Eq. (8).

$$A^*/C^{0*}_D = \frac{K^*_1(1-A^*)}{(1+K^*_1)[1-(K^*_1A^*/1+K^*_1)]} = Y_1(A^*) \qquad ...(8)$$

Expanding $Y_1(A^*)$ in terms of A^* by Taylor's expansion gives,

$$A^*/C^{0*}_D = \frac{K^*_1}{1+K^*_1} - \frac{K^*_1}{(1+K^*_1)^2}.A^* + R_1(A^*) \qquad ...(9)$$

where

$$R_1(A^*) = -\frac{1}{1+K^*_1-K^*_1A^*}\left(\frac{K^*_1A^*}{1+K^*_1}\right)^2 \qquad ...(10)$$

$R_1(A)^*$ represents the higher order correction terms. It should be noticed that Eq. (9) reduces to Eq. (7) only when $K_1 \ll 1$. From the above derivation, we can see that the linear relation given by Eq. (9) represents the tangent to the curve A^*/C^{0*}_D versus A^* at $A^* = 0$.

From Eq. (8) it is clear that as long as K^*_1 (the product of the equilibrium constant and the initial concentration of acceptor) is kept small so that $(K^*_1A^*/(1+K^*_1)^2$ is within the experimental accuracy (smaller than unity), a good linear relation between A^*/C^{0*}_D and A^* is expected to hold regardless of the donor concentration used. Fig. 2 shows the theoretical relation between A^*/C^{0*}_D and A^* for different K^*_1 values. An analysis of these plots indicates that the linear relation between A^*/C^{0*}_D and A^* holds only up to $K^*_1 \approx 0{\cdot}02$, above which the plot starts deviating from linearity at lower concentration of the complex as observed previously also in our NMR investigation[5], but linearity is observed at higher concentration of the complex (Fig. 2).

To compare the best theoretical linear relation between A^*/C^{0*}_D and A^* with the conventional linear relation between A^*/C^{0*}_D and A^*, we write Eq. 7 as

$$A^*/C^{0*}_D = K^*_1(1-A^*) + R_{1H}(A^*) \qquad ...(11)$$

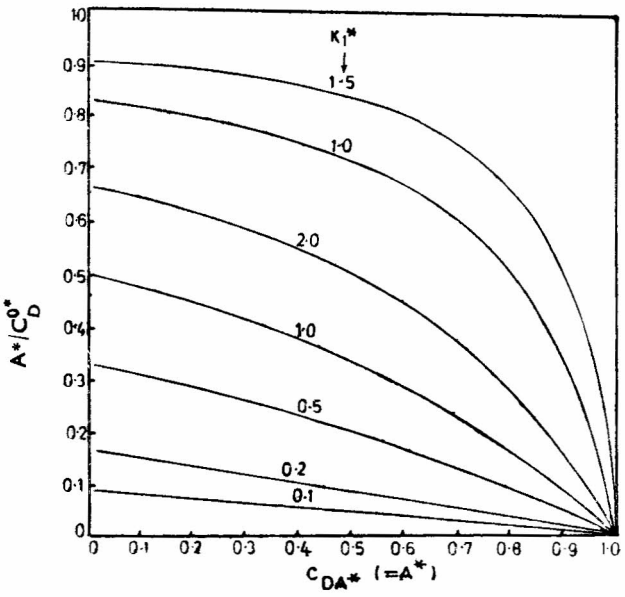

Fig. 2 — Theoretical plots of A^*/C^{0*}_D against A^* for different values of K^*_1

where the correction term $R_{1H}(A^*)$ is given by Eq. (12).

$$R_{1H}(A^*) = -K^*_1(1-A^*)(A^*/C^{0*}_D) \qquad ...(12)$$

or

$$R_{1H}(A^*)/(A^*/C^{0*}_D) = -K^*_1(1-A^*) \qquad ...(13)$$

which should be compared with

$$\frac{R_{1H}(A^*)}{A/C^{0*}_D} = -\frac{K^*_1}{1-A^*}\left(\frac{A^*}{1+K^*_1}\right)^2 \qquad ...(14)$$

Thus, from Eqs. (13) and (14) we can determine the errors introduced by the BH, Scott or FHW models and by the exact linear relation.

It can easily be shown that the linear relation given by Eq. (11) actually represents the tangent to the curve representing plot of A^*/C^{0*}_D versus A^*, at $A^* = 1$, if we notice that $Y^1_1(1) = -K^*_1$, and A^*/C^{0*}_D equals zero at $A^* = 1$. A theoretical comparison of the relation between A^*/C^{0*}_D and A^*, generated by Eqs. (7), (8) and (9) for different K^*_1 values is shown in Fig. 3. It may be seen from this figure that the FHW equation and the exact linear relation behave in a similar manner and are in good agreement with the exact theoretical relation only when K^*_1 is smaller than 0·01. As K^*_1 increases, both plots deviate from the exact theoretical plot, and it can be noticed that in the FHW model Eq. (11) represents the tangent to the curve representing the plot of A^*/C^{0*}_D versus A^*, at $A^* = 1$. Eq. (9) represents the tangent at $A^* = 0$ as shown above.

Results and Discussion

Spectrophotometric equilibrium data based on BH model for some fairly strong molecular complexes of iodine with different donors[6-16] are summarized in Table 1. The data obtained using our model (Eq. 15) and the percentage error introduced in each case have also been shown in Table 1. It is

TABLE 1 — COMPARISON OF SPECTROPHOTOMETRIC EQUILIBRIUM DATA FOR SOME STRONG 1:1 MOLECULAR COMPLEXES OF IODINE* WITH DIFFERENT DONORS

Donor	Literature values			Calc. values from Eq. 15		Percentage error	
	K (litre mole^{-1})	ϵ_{max}	Ref.	K (litre mole^{-1})	ϵ_{max}	K	ϵ_{max}
N,N-Dimethylaniline	18·8	—	7	19·8	—	5·05	—
Methylamine	530·0	—	8	551·8	—	3·95	—
Ethylamine	720·0	—	8	762·1	—	5·50	—
Tri-*n*-propylamine	1390·0	—	8	1560·5	—	10·90	—
Tri-*n*-butylamine	1600·0	—	8	1820·8	—	11·02	—
Triethylamine	6320·0	—	9	15369·0	—	58·80	—
Dimethylamine	6800·0	—	8	22495·0	—	69·70	—
Phthalazine	346·7	—	10	574·5	—	39·60	—
Diethylsulphide	210·0	—	11	235·8	—	10·90	—
Pyridine	269·0	—	12	302·7	—	11·12	—
$Be(acac)_2$	10·1	2718	5	12·4	2729	18·50	0·40
$Sc(acac)_3$	20·0	25770	5	21·8	26040	8·25	1·04
$Al(acac)_3$	76·1	6410	5	81·3	6627	6·30	3·20
Hexamethylbenzene	148·0	4780	13	164·2	4806	9·08	0·54
N,N-Dimethylacetamide	2·6	760	14	2·7	779	4·40	2·45
$Th(acac)_4$	—	3472	5	—	7264	—	52·20
$Zr(acac)_4$	—	3390	5	—	6728	—	49·60
N,N-Dimethylpropionamide	—	704	15	—	719	—	2·08
Dioxane	—	937	16	—	946	—	0·97
Triethylamine	—	2560	9	—	3040	—	15·78

*$C_A^0 = 3{\cdot}64\times10^{-6}M$ for Sl No. 1-7, 14, 20; $5{\cdot}0\times10^{-4}M$ for Sl No. 8; $2{\cdot}51\times10^{-4}M$ for Sl No. 9, 10; $4{\cdot}0\times10^{-4}M$ for 11, 13, 16, 17; $9{\cdot}2\times10^{-3}M$ for Sl No. 15.

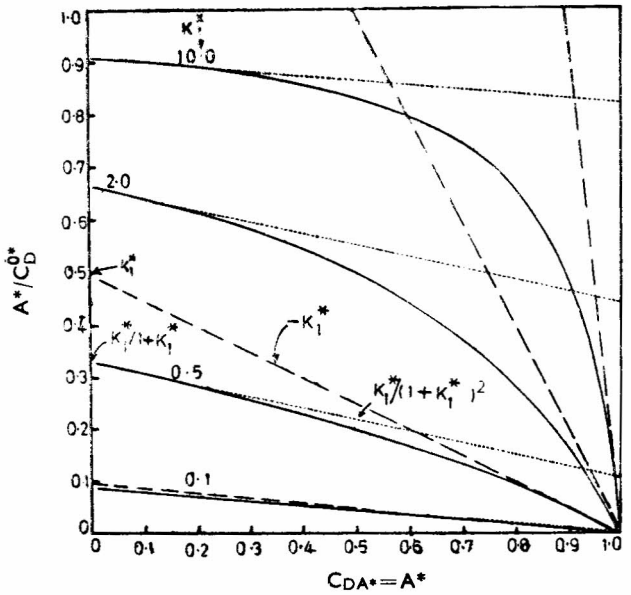

Fig.3 — Comparison of theoretical relationship between A^*/C_D^{0*} and A^* for different values of K_1^* using different models [Continuous line, exact linear equation; broken line, Foster-Hammick-Wardley equation; dotted line, present equation]

apparent from these data that the percentage error becomes larger when the product of K_1 and C_A^0 becomes more pronounced compared to unity, as is evident from Eq. (9) which may be represented after neglecting the higher order correction terms as follows:

$$A/C_D^0 = K_1C_A^0\epsilon/(1+K_1C_A^0) - K_1A/(1+K_1C_A^0)^2 \quad ...(15)$$

Adoption of the present model (Eq. 15) introduces errors varying from 4 to 70% in K_1 and from 1 to 50% in ϵ for the present complexes. In the case of fairly strong triethylamine-iodine complex, approximately 10% error in K_1 was introduced by the equation suggested by Nagakura[9]. For this particular system 58·8% error in K_1 is observed on the basis of present model (Table 1). Though LaBudde and Tamres[17] have proposed a means of estimating the errors introduced by dropping terms through linear regression model, our model (Eq. 15) would be helpful to calculate the errors introduced in BH, Scott or FHW equations and further it will provide a convenient graphical approach for determining K_1 and ϵ of molecular complexes in general and those of fairly strong molecular complexes in particular.

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